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Energy Procedia 2 (2010) 243–250

**Energy
Procedia**www.elsevier.com/locate/procedia

E-MRS Spring meeting 2009, Symposium B

Structural studies of multilayered Ge nanocrystals embedded in SiO₂ matrix fabricated using magnetron sputtering

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Received 1 June 2009; received in revised form 1 December 2009; accepted 20 December 2009

Abstract

Ge nanocrystals (Ge NCs) were grown in a multilayered superlattice structure using magnetron co-sputtering technology. Studies were taken to optimize the processing conditions including post-annealing temperature and duration. Structural properties of Ge NCs and multi-bilayers, such as crystallization process, precipitate crystallinity, size-control of nanocrystals and influence of interlayer diffusion, were particularly chosen to be investigated. The experimental results indicated that high quality and reproducible multilayered Ge NCs can be obtained with an appropriate thermal annealing condition. This investigation builds a technical foundation for fabrication of tandem solar cell applicable Ge NCs absorber films.

© 2010 Published by Elsevier Ltd Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).*Keyword:* Germanium; nanocrystals; quantum dots; SiO₂ matrix; superlattice; size-control; co-sputtering; tandem solar cells

1. Introduction

As one of the low dimension structures based on group IV semiconductor materials, Germanium nanocrystals (Ge NCs) embedded in dielectric matrix have attracted increasing research interest during last decade because of its potential to be utilized in electronic and optoelectronic devices [1-3]. Ge NCs are also believed to be promising as an alternate Si-process compatible technique for thin film tandem solar cells due to its relatively low process temperature. To the best of our knowledge, the most widely investigated approach so far is a single layer structure with Ge NCs randomly dispersed in a SiO₂ matrix. This simple structure is easy to process and has been realized by various technologies, such as co-sputtering [2], hydrothermal oxidation [4], and chemical vapor deposition [5] *etc.*. However, despite the intensive studies in this area, the single layer structure still suffers from not having accurate control of size, position, shape and density of nanocrystals in the films.

Recently, a multilayer superlattice approach has been developed in our research centre to achieve more uniform size and distribution of nanocrystals [6]. The Ge NCs fabricated using this method exhibited a fairly uniform size

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and were equally spaced in the multilayer growth direction [7]. Compared to bulk Ge, the nanocrystals showed blue shifts in both optical absorption band gap and photoluminescence (PL) peak energy, which was likely to be attributed to the quantum confinement effect [8]. Further study demonstrated a modulation of average crystallite size by altering the thickness of active layers containing Ge NCs. Size variations evidently resulted in corresponding changes of optical absorption and PL characteristics [9].

The investigation in this paper was undertaken in order to find optimal processing conditions of multilayered Ge NCs, in particular with respect to their structural characteristics. The effects of post-annealing temperature and duration on the crystallization of Ge precipitate and the process of nanocrystal growth were discussed based on Raman spectroscopy and X-ray diffraction measurements. The evolution of interlayer diffusion in multi-bilayers during annealing was briefly probed by X-ray reflection measurements. Such an investigation is rather important in establishing an appropriate technical foundation to provide high quality and consistent material for accurate optical and electrical characterisation in future work.

2. Experiments

The multilayered superlattice structures were deposited on silicon substrates by co-sputtering using an RF-magnetron apparatus. The sputtering target was a circular fused quartz partially covered with several pieces of high purity (99.9999%) Ge strips. The concentration of Ge precipitate in the film was controlled by the number of mounted strips. The target-substrate distance was about 8 cm. The base pressure of the chamber was 3.0×10^{-4} Pa and the multilayer films were deposited at 25 W RF power under room temperature. The Ge-rich SiO_2 (GeRO) layer and $\text{GeO}_2/\text{SiO}_2$ layer were alternately deposited by Ar sputtering with a partial pressure of 0.1 Pa and by reactive sputtering with a mixed gas of Ar and O_2 with a partial pressure of 0.2 Pa, respectively, resulting in a multi-bilayer structure. All the samples in this study had 10 bi-layers and the deposition time for both GeRO and $\text{GeO}_2/\text{SiO}_2$ layers were 6 minutes (min). In situ cleaning of the target using Ar plasma was carried out before deposition of GeRO layers to ensure that GeO_x formed on the Ge strips during reactive sputtering was removed. A thick $\text{GeO}_2/\text{SiO}_2$ capping layer was grown at the top of the structure to prevent possible oxidation of Ge during thermal annealing and penetration of moisture. At last, thermal annealing was used to crystallize Ge NCs in vacuum. The effect of annealing temperature was examined by varying the temperature from 620 °C to 720 °C with fixed annealing duration of 40 min. On the other hand, the effect of annealing duration was also examined by varying the duration from 6 min to 25 min with fixed annealing temperature of 685 °C.

The multilayered structure was investigated by transmission electron microscopy (TEM). Raman scattering spectra were obtained by micro-Raman spectroscopy in a backscattering configuration to qualitatively examine the degree of crystallization of the films. The beam was excited by the 514.4nm line of an Ar laser with a spectral resolution of $1\text{--}2\text{cm}^{-1}$. The crystalline properties of the films were collected using glancing incidence X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation ($\lambda=0.154\text{nm}$), running at a voltage of 45kV and a current of 40mA. The glancing angle between the incident X-ray beam and the sample surface was set at 0.30 degree, very close to the critical angle for total external reflection. In addition, the X-ray reflection measurement using the same apparatus and setup was used to characterize the multilayered structure.

3. Results and discussion

The multilayered superlattice structure fabricated in our experiments is shown in Fig. 1(a). A corresponding cross-sectional TEM image of the three bi-layers is also shown in Fig. 1(b). We can clearly see the alternate GeRO layer and $\text{GeO}_2/\text{SiO}_2$ layer. However, vague interfaces are noticed between GeRO and $\text{GeO}_2/\text{SiO}_2$ layers, indicating that interdiffusion phenomenon happens in the sample. It is known that thermal annealing contributes to the interdiffusion process. Significant interdiffusion can dramatically blur the interface and deteriorate the superlattice structure. Therefore, it is important to choose optimal annealing parameters to retain good multilayer structure without sacrificing the nanocrystal quality.

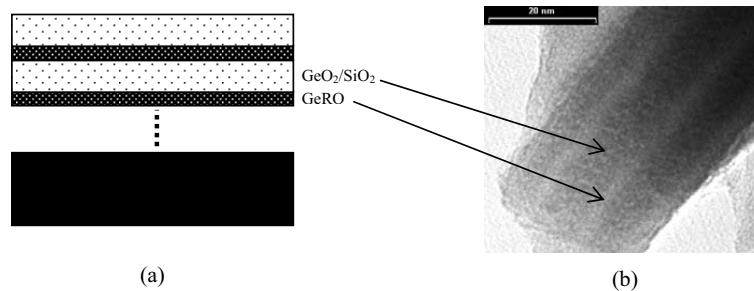


Figure 1. (a) Schematic diagram of multilayered superlattice structure, (b) cross-sectional TEM image of sample annealed at 685 °C for 40 min. The sample has 3 bi-layers and the deposition time for GeRO and GeO₂/SiO₂ layers is 3 min and 6 min, respectively. The thickness of GeRO and GeO₂/SiO₂ layers is $\sim 3.6 \pm 0.2$ nm and 7.8 ± 0.2 nm.

Fig. 2 shows the Raman spectra of the samples with different annealing temperatures. The samples show Raman active mode near 300 cm^{-1} , which corresponds to the TO-LO phonon mode of crystalline Ge [10]. All the spectra show broadening and asymmetric shoulder in the lower wavenumber tail. This asymmetric peak broadening can be interpreted by the folding of optical phonons in nanocrystals which allows phonons of lower energy to be optically active at zone centre [11]. These features strongly indicate the formation of Ge NCs in SiO₂ matrix at annealing temperatures down to 620 °C.

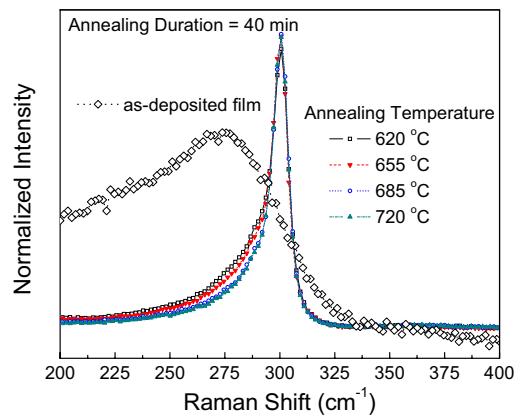


Figure 2. Raman spectra of samples annealed at different temperatures for 40 min. The spectra of as-deposited film was also included.

To quantitatively understand the crystallization process of Ge precipitate, the Raman spectra are decomposed into three Gaussian peaks corresponding to the crystalline peak around 300 cm^{-1} , the intermediate peak around 292 cm^{-1} , and the non-crystalline peak around 270 cm^{-1} . The intermediate component is usually associated with the small nanocrystalline grains of dimension in the range of less than 3 nm [12]. The fitted Raman spectra are listed in Fig. 3. The Raman peak from the sample annealed at 720 °C can be well fitted with these three components. However, we obtain a poorer fit to the Raman peak of samples annealed at lower temperatures, which may be due to a larger size

distribution in the samples. Fig. 3 also shows a decrease in non-crystalline component as well as intermediate component with increasing annealing temperature. This indicates a gradual transition from non-crystalline phase to crystalline phase.

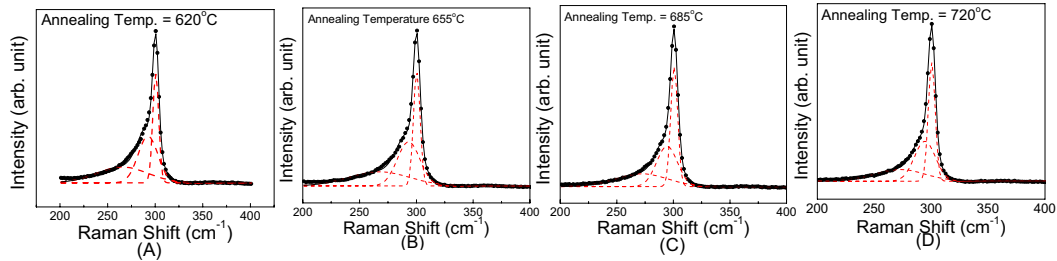


Figure 3. The Raman spectra from samples and fitted with three Gaussian peaks. Samples were annealed at (a) 620 °C, (b) 655 °C, (c) 685 °C and 720 °C, respectively and the annealing duration was 40 min for all samples.

Considering intermediate component as portion of crystalline component, the volume fraction of crystallinity F_c can be simply calculated using equation 1 [13]:

$$F_c = \frac{I_c + I_m}{I_c + I_m + \beta I_{nc}} \quad (1)$$

where I_c , I_{nc} , and I_m are the integrated intensities of the crystalline, non-crystalline, and intermediate components, respectively. β is the ratio of the cross section of the non-crystalline phase to the crystalline phase. For simple calculation, we use the β value of unity which is appropriate for crystallites of a few nm in size [14]. Fig. 4 represents the increase of F_c with the annealing temperature. Higher F_c is obtained at higher temperatures indicating that more Ge precipitate is transformed from non-crystalline state to crystalline state. However, F_c value is still less than 75% even at the highest annealing temperature. This low volume fraction of crystallinity implies that a significant amount of excess non-crystalline Ge co-exists with Ge NCs in the active GeRO layers at our chosen annealing condition. To avoid this undesirable non-crystalline Ge residue, one possible approach is to reduce the Ge coverage on the quartz plate, hence reducing the concentration of Ge precipitate in the deposited film.

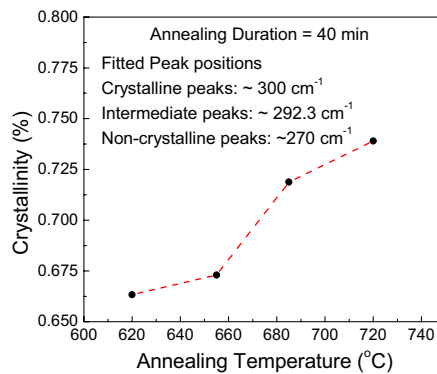


Figure 4. Volume fraction of crystallinity of samples annealed at different temperatures.

The crystallization process is also investigated in terms of annealing duration. The Raman spectra of samples annealed at 685 °C for different annealing durations are shown in Fig. 5. The crystallization of Ge is found to happen within the first 6 min of annealing. Nevertheless, a noticeable amorphous hump is observed in the Raman spectra of sample annealed only for 6 min, suggesting an early stage of crystallization process. When the annealing duration is increased, we see sharper and narrower phonon peaks of crystalline Ge, and the amorphous peak is gradually weakened. Particularly, the difference of Raman peaks becomes negligible for annealing durations longer than 15 min. It is concluded that increasing annealing temperature or annealing duration will both give rise to the increase of Ge crystallinity when the annealing temperature is higher than the crystallization temperature of Ge which is about 400 °C [15]. In fact, this is not very surprising if we realize that nanocrystals or clusters in our samples were formed by diffusion of Ge atoms or clusters in SiO₂ matrix.

X-ray diffractograms using glancing angle incidence have been obtained from both sets of multilayer films and are presented in Fig. 6. The penetration depth of incident X-ray source is larger than the thickness of samples, so all measured information is averaged throughout the whole film. All samples show three characteristic Bragg peaks

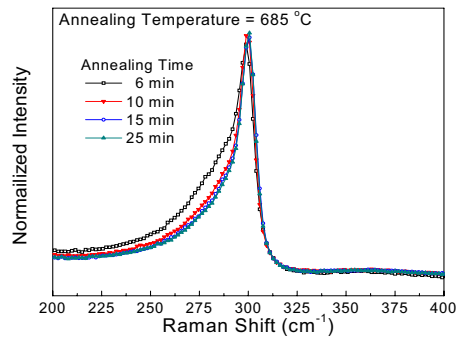


Figure 5. Raman spectra of samples annealed at 685 °C for different durations.

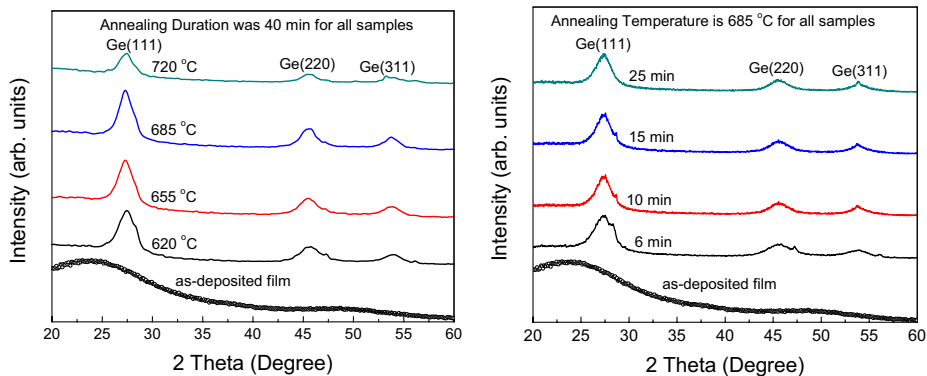


Figure 6. Glancing incidence X-ray Diffraction image of (a) samples annealed at different temperatures for 40 min, and (b) samples annealed at 685 °C for different durations. The pattern of as-deposited film was also included.

of crystalline Ge, which can be associated with the groups of crystalline planes $\{111\}$, $\{220\}$ and $\{311\}$. This confirms the good crystallinity of the Ge phase in the multilayer samples, which is consistent with Raman results. The average sizes of Ge NCs can be estimated from the $\{111\}$ Bragg peaks using the Scherrer equation [16].

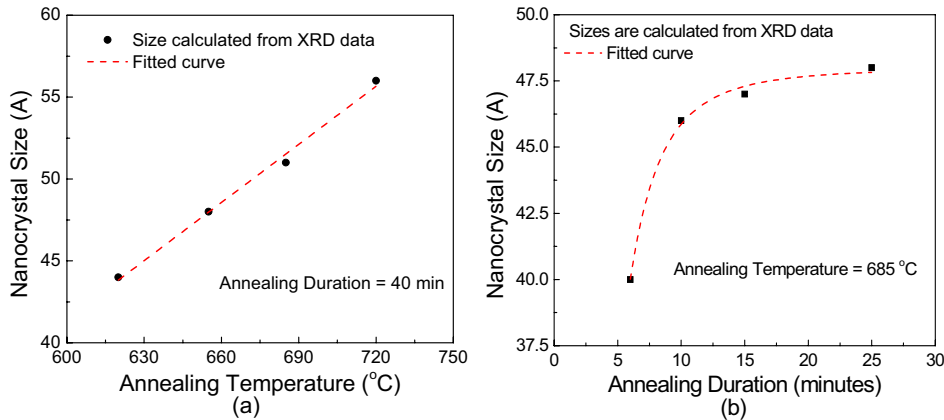


Figure 7. Ge NCs' sizes of (a) samples annealed at different temperatures for 40 min, and (b) samples annealed at 685 °C for different durations. The nanocrystal size is calculated from Bragg peaks of $\{111\}$ plane using Scherrer equation.

The dependence of nanocrystal sizes on annealing temperature and durations are presented in Fig. 7. Increasing either temperature or duration leads to increase in the nanocrystal size. This agrees well with the growth process by diffusion of neighboring Ge atoms. The Ge NC size increases dramatically from ~ 4.4 to ~ 5.6 nm when annealing temperature increases from 620 °C to 720 °C. Therefore, the size of Ge NCs in our sample is very sensitive to the annealing temperature.

In Fig. 7(b), we notice that the size increase begins to level off after 15 min, indicating that the nanocrystals approach the upper limitation of size. This size constraint effect is also observed in the growth of Si NCs in a SiO/SiO₂ superlattice [17]. In the superlattice structure studied here, the GeO₂/SiO₂ spacing layers work as barrier layers to the crystal growth in the direction of multilayer growth. With specific annealing conditions (sufficient temperature and duration), Ge tends to precipitate nanocrystals of a diameter approximately close to the original thickness of GeRO layer. In contrast, this leveling off phenomenon is not observed in Fig. 7(a). Comparing the sample annealed at 685 °C for 40 min from Fig. 7(a) and the sample annealed at 685 °C for 25 min from Fig. 7(b), the former has a crystallite size only slightly larger than that of the latter. This agrees well with our discussion on size control effect of superlattice structure. However, when annealing temperature ramps up to 720 °C, the nanocrystal size further increases to 5.6 nm. We propose that this can be related to the enhanced interdiffusion between layers of the multilayer structure, hence reducing the controllability of crystallite size. At higher annealing temperature enhanced interdiffusion results in rougher interface between GeRO layer and neighboring GeO₂/SiO₂ layer. This explanation is verified by the specular X-ray reflection measurements. Fig. 8(a) shows that Bragg peaks become weaker and the peaks labeled in red circles disappear at higher annealing temperature, indicating a degradation of the roughness at the interface of successive layers. On the other hand, patterns in Fig. 8(b) exhibit nearly the same features, indicating that the layer interface remains almost unchanged for extended annealing duration. Therefore, we tentatively consider that increasing annealing temperature will more effectively cause interdiffusion between GeRO layers and GeO₂/SiO₂ spacing layers rather than increasing annealing duration.

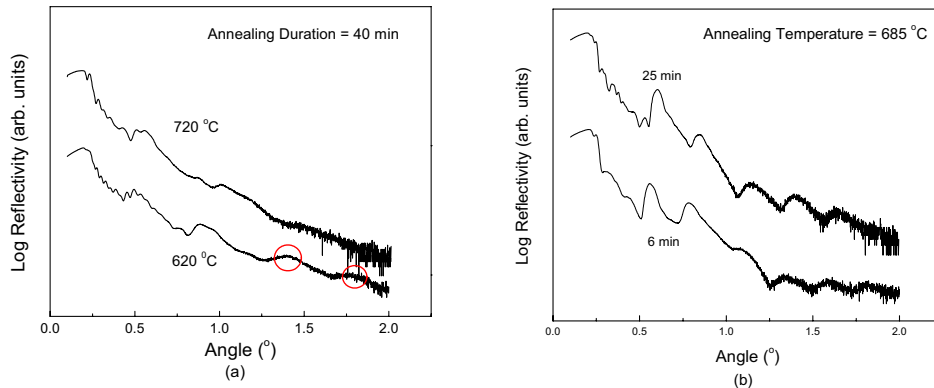


Figure 8. XRR patterns of (a) samples annealed at 620 °C and 720 °C for 40 min, and (b) samples annealed at 685 °C for 6 min and 25 min.

4. Conclusion

Ge NCs embedded in SiO₂ matrix were prepared in a superlattice structure using magnetron co-sputtering followed by vacuum thermal annealing. The influence of annealing temperature and duration on the formation of Ge NCs was comprehensively studied by Raman spectroscopy, X-ray diffraction and reflection. The experimental results revealed the growth process of Ge NCs and the change of multilayer structure during annealing. With increasing annealing temperature and duration, more Ge changed from amorphous phase to nanocrystalline phase. Crystallinity calculated by deconvolution of Raman spectra indicated that significant amount of non-crystalline Ge existed in the annealed films at our chosen conditions. The average size of Ge NCs increased with both annealing temperature and duration. The growth of nanocrystals was found to be confined by the GeO₂/SiO₂ spacing layer. At higher annealing temperature, more significant interdiffusion resulted in rougher layer interface between GeO₂ and GeO₂/SiO₂ layers, which weakens the size controllability of the superlattice structure.

Our experimental findings suggest that carefully chosen annealing parameters are critical in order to obtain films having both high quality Ge NCs and a multilayered superlattice structure. This study is very useful for optimization of the process conditions for high quality and reproducible Ge NCs for future optical and electrical characterisation.

5. Acknowledgement

This work was supported by the Australian Research Council (ARC) via its Centre of Excellence scheme and by the Global Climate and Energy Project (GCEP) administrated by Stanford University. Bo Zhang thanks the Asia-Pacific Partnership on Clean Development and Climate and IDP Education Australia for supporting his study in Australia.

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